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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/EP89/01610 (22) International Filing Date: 20 December 1989 (20.12.89) (71) Applicant (for all designated States except US): ATLAS COPCO AIRPOWER N.V. [BE/BE]; Boomsesteenweg 957, B-2610 Wilrijk (BE). (72) Inventor; and (75) Inventor/Applicant (for US only) : GAUGER, Jürgen [CH/CH]; Chemin des Mésanges 34, CH-1226 Genève (CH). (74) Agent: JOHANSSON, Lars; Cerac S.A., Chemin des Larges Pièces, CH-1024 Ecublens (CH). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.		Published <i>With international search report.</i>
(54) Title: A METHOD FOR DRYING OF GASES, ESPECIALLY COMPRESSED AIR, A MEMBRANE FOR CARRY- ING OUT SAID METHOD AND A PROCESS FOR THE MANUFACTURING OF SAID MEMBRANE (57) Abstract A method for drying of gases, especially compressed air, by means of a membrane having a thin membrane coating with a certain separation factor (water vapor-gas) arranged on a membrane support whereby gas or air containing water in vapor form is applied to one side of the membrane, the feed side, and due to the separation factor mainly water vapor is permeating to the other side of the membrane, the permeate side. A fraction of the gas or air stream, is arranged to permeate through the membrane from the feed side to the permeate side, in order to transport permeated water vapor away from the permeate side of the thin membrane coating and through the membrane support, thereby creating and maintaining a water vapor partial pressure difference between the feed side and the permeate side of the thin membrane coating, which constitutes the driving force for the permeation of the water vapor through the membrane. The membrane coating comprises a high surface area filler. Process for the manufacturing of the membrane where said filler is mixed with at least a part of the membrane forming liquid in a wet-milling process.		

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A METHOD FOR DRYING OF GASES, ESPECIALLY COMPRESSED AIR, A
MEMBRANE FOR CARRYING OUT SAID METHOD AND A PROCESS FOR THE
MANUFACTURING OF SAID MEMBRANE

5

This invention refers to a method for drying of gases,
especially compressed air, a membrane for carrying out said
method and a process for the manufacturing of said
membrane. The membrane comprises a thin membrane coating
10 with a certain separation factor (water vapor - gas)
arranged on a membrane support. Gas or air containing water
in vapor form is applied to one side of the membrane, the
feed side, and due to the separation factor mainly water
vapor is permeating to the other side of the membrane, the
15 permeate side.

Traditionally gases, including compressed air, are dried
for industrial purposes by means of one of the following
methods.

20

In the refrigeration-drying method the gas or air,
containing water in vapor form, is cooled down to a
temperature at which the water can condense. In this
continuous method the condensed water is then taken out of
25 the system in liquid form. By means of this method dew
points down to about 1°C could be reached. The equipment
needed for carrying out the method in an industrial scale
is quite bulky and energy consuming. Moreover the method
does not conveniently give the possibility to produce gases
30 with dew points lower than 0°C.

The other commonly used method is an adsorption method.
This is a capacitive type drying method making use of
certain types of zeolites and other adsorbents like silica
35 gel and activated alumina, which are fine particle
materials having a large active surface area.

In a simple realisation of this method the gas or air to be dried is supplied to a first column or tower containing adsorbent material. The water contained in the gas is hereby adsorbed loading the material with water vapor. At the same time an exhausted second column or tower of the same type is regenerated. Conduits, valves and a control system makes it possible to switch the gas streams between the two vessels. Thereafter the process is repeated. Due to the need of two pressure vessels, valves and the control system adsorber dryers are quite complex and costly.

The regeneration can be done in different ways. One way would be by means of the so called temperature-swing-method (TSA) which means that the temperature of the adsorber-bed in the regeneration phase of the process is increased in order to desorb the humidity. Another way to regenerate the adsorbing material is used in the so called pressure-swing-method (PSA). Instead of raising the temperature in the regeneration phase the adsorbing material is exposed to a lower pressure.

Dew points of -20°C - -40°C or even lower can be obtained by means of this method with zeolites or other adsorbents if the adsorption properties of the material is used to its limits. This induces, however, extensive energy losses, in the TSA-method, due to the temperature requirement in the regeneration phase.

In a realisation of a continuous process (Munters dryer) of basically the same idea, the adsorbing material is arranged on the inner surface of coaxial channels in a drum which drum is rotated inside a pressure vessel. The gas-stream to be dried is arranged to pass inside the channels of one part of the drum whereby the humidity is adsorbed. At the

same time the other part of the drum is heated for the desorption of the humidity.

5 A disadvantage with these methods is that the realisation in an industrial scale is quite bulky. When applying the TSA- or PSA-methods to the drying of compressed air, at least two pressure vessels are needed, in the system installation, including, as mentioned above, the necessary conduits, valves and the control system for switching the
10 flow of the gas through the system. Additionally, these methods imply a considerable energy loss especially in the regeneration phase. In the TSA-method the loss is mainly due to the heating or pressure loss (Munters dryer) and in the PSA-method due to loss of gas.

15

A neighboring technical field relates to the separation of gases from mixtures of gases by means of membranes. Several methods and corresponding special membranes are known for this purpose.

20

US-A-4230463, for example, discloses a multicomponent membrane for gas separation, comprising a coating in contact with a porous separation membrane, wherein the separation properties of the multicomponent, or composite,
25 membrane is principally determined by the porous separation membrane as opposed to the material of the coating. This is achieved by choosing a coating material, e.g. from the group polysiloxanes which exhibits less resistance to permeate gas flow than the porous support material, e.g.
30 polysulfone. The support material, however, has a better separation factor and therefore determines the efficiency of the gas separation. Since the support has also a higher resistance to the gas flow, it practically also determines the flux rate. The beneficial effect of the coating is
35 therefore mainly the occlusion of the pinholes and the protection of the polysulfone membrane against damages

during handling and assembly in modules. Flux rate and separation factor are the most essential parameters for membranes used for gas separation.

- 5 It is also known membranes for gas separation having, as a filler or in a thin top layer on the membrane, active material increasing the separation properties of the membrane. The active material used in this connection is typically zeolites, natural and synthetic.

10

In the French patent FR-A-2079460 is disclosed a membrane containing natural or synthetic zeolites as filler and a gas separation process making use of this membrane. In this membrane the capacative properties of the active material
15 is utilised. The process has, as the capacitive processes described above, two phases, one adsorption phase and one regeneration phase. Two different processes are disclosed, one of the batch type in which two different membranes are used and the other of a continuous type making use of only
20 one membrane. In the continuous process the single membrane in the form of a band is physically moved over rollers between two containers one for each of the phases of the process.

- 25 Membranes and processes for pervaporation are also known. Such a membrane is disclosed in the European Patent Application EP-A-254758. This membrane comprises an elastomer polymer matrix containing zeolite. The membrane is optimised for the permeation of alcohol, and therefore
30 the zeolites have to be as hydrophobic as possible. In general pervaporation membranes, like other membranes working with liquid feeds, e.g. reverse osmosis membranes, are not defectfree enough to be used for gas separation.

- 35 Membrane processes have also been developed for removing water vapor from gas-vapor mixtures. EP-A-308002, e.g.

discloses a method and a membrane for this purpose. A cellulose or cellulose acetate film is impregnated with a hygroscopic electrolyte in order to increase the flux rate. Interesting short term performances have been observed with
5 this type of membrane. However, cellulose and cellulose acetate membranes have important drawbacks concerning long term stability. They are e.g. very sensitive to hydrolytic degradation, bacteria growth and crack formation due to large dimensional changes during transitions from the dry
10 to the wet state.

One object of the present invention is to provide a method for drying of gases, especially compressed air by means of a membrane which method is characterised in that gas or
15 air, is arranged to permeate through the membrane from the feed side to the permeate side, in order to transport permeated water vapor away from the permeate side of the thin membrane coating and through the membrane support, thereby creating and maintaining a water vapor partial
20 pressure difference between the feed side and the permeate side of the thin membrane coating, which constitutes the driving force for the permeation of the water vapor through the membrane.

One important advantage with a method according to the
25 invention is that the permeation of gas through the membrane, controlled by the properties of the membrane coating, stabilizes the partial pressure difference between the feed side and the permeate side of the membrane coating without the help of a sweep gas or a vacuum which are the
30 currently used methods.

In the method making use of a sweep gas the permeate side of the membrane is swept with dry air e.g. an expanded part of the dried product air which is fed in a counterflow
35 manner towards the permeate side of the membrane. Hereby an important part of the dried product air is lost which

represents a corresponding important loss of energy and moreover the method is not very efficient due to the fact that the dry sweep air only contacts the backside of the membrane support and not the membrane layer itself.

5 Therefore, a diffusion gradient between the feed side membrane and the permeate side support surface is established which diminishes the performance of the membrane.

10 The method making use of a vacuum on the permeate side of the membrane gives good drying efficiency but is not economic for drying of compressed air in an industrial scale due mainly to the high investment and operation costs of the necessary vacuum pump.

15

Another object of the invention is to provide a membrane specially designed for carrying out said method characterised in that said membrane coating comprises silicon elastomer and 30-90 % of an active filler.

20

It is well known that silicone elastomers and especially polydimethylsiloxane (PDMS) has a very high permeability for water vapor. However, a membrane made from unmodified PDMS does not give economically interesting results for the
25 drying of most gases, e.g. compressed air, since the gas (air) loss is too high due to the poor selectivity of the membrane.

The advantages with a membrane according to the invention
30 is that modules and systems for the drying of compressed air can be designed which are less bulky, cheaper, work in a continuous process i.e. without any regeneration and consequently do not need any complex regulation systems and valves.

35

Further, an essential feature of the membrane according to the invention is that the gas or air which is allowed to permeate the membrane in order to push away the water vapor from the permeate side has a composition close to the product air or gas. A membrane designed for the drying of compressed air e.g. would consequently deliver a product air having a content of oxygen still within the limits prescribed for breathing air. A too high separation of oxygen from the air might cause problems in a number of applications e.g. when the air is to be used by dentists or in other applications in which breathing of the product air is involved.

Further, the membrane according to the invention has a low degree of swelling in contact with water vapor which together with the elastomeric properties of the PDMS is essential in order to avoid crack formation when the dryer is used intermittently. Mechanical properties, even in the hydrated state, reliability and life time are excellent.

A further object of the invention is to provide a method for manufacturing of the membrane according to the invention.

A general problem with the manufacturing of membranes containing fillers is to achieve a homogeneous membrane. The fillers are by necessity small particle, large active surface materials which very easily agglomerate due to considerable internal forces between the particles. If the membrane is thin e.g. in the order of a few particle diameters the homogeneous distribution of the filler is even more difficult.

The method for manufacturing of membranes according to the present invention provides a solution to this problem. In a preferred embodiment the filler is milled in the wet state

together with the membrane material and optionally with a hardener for the membrane material and/or a dilution agent. In this way a very homogenous thin membranes could be achieved.

5

In stead of wetmilling high speed agitation under wet conditions could be used.

Further advantages and characteristics of the invention
10 will be apparent from the following description.

As described above the loss of energy, in one or the other form, constitutes an essential drawback with the methods for drying of compressed air. The application of membrane
15 technology to this technical field might seem promising at first sight and the development so far has been in the direction of membranes having higher separation factors water vapor- gas. This means that the build- up of water vapor on the permeate side of the membrane has to be dealt
20 with to maintain the partial pressure difference. The two commonly used methods to do this have already been mentioned above.

The method for drying of gases according to the present
25 invention addresses this problem in a quite different way. In stead of looking for an even more perfect membrane when it comes to the separation factor water vapor- gas in order to allow, if possible, only water vapor to permeate through the membrane, the method according to the invention makes
30 use of a special membrane having a controlled, optimized permeation rate for the gas or air. The amount of gas or air allowed to permeate through the membrane is just enough to transport the permeated water vapor away from the permeate side of the membrane coating and through the
35 support, thus enabling a stabilization of the partial pressure difference over the membrane coating. It has been

shown that certain active fillers which limit the air loss maintain or even increase the flux rate for the water vapor.

- 5 This means that the process step according to the prior art methods of removing by means of a sweep gas or vacuum the water vapor from the permeate side of the membrane can be abolished.
- 10 By choosing certain combinations of parameters of the membrane e.g. fluxrate, separation factor etc. by controlling mainly the choice of filler material and the percentage of filler in the membrane layer, a method for drying of gases is created which according to the above
- 15 gives a dry product air having essentially the same composition as natural air with corresponding advantages.

The frequent start-up and shut-down of compressed air dryers used in industry represents a very tough condition

20 for a membrane dryer. The more or less hydrophilic membrane shrinks and swells frequently which might develop cracks which would cause the dryer module to leak and loose its performance.

- 25 Due to the new method for drying of compressed air according to the invention in combination with the specially designed new membrane, according to the following description, membrane technology could be applied with very good long term stability in intermittently operated drying
- 30 installations..

The specially designed membrane could use as a support material a chemically and mechanically resistant micro-porous polymer material which could be a commercially

35 available ultrafilter or microfilter of polysulfone,

polyethersulfone, polyamide or polypropylene. Said support could be applied in form of flat sheets or hollow fibres.

The diameter of the pores in the case of an ultrafiltration
5 membrane would be about 10 000 to 1 000 000 daltons and between about 0.01 to several microns in the case of a microfilter.

In a preferred embodiment a polyamide microfilter with a
10 pore diameter of 0.01 to 1 micron was used.

As a material for the coating commercially available liquid
silicones on the basis of polydimethylsiloxanes has been
used together with liquid hardeners. Such silicones in
15 combination with hardeners are sold for instance by the company DOW CORNING (USA), UNION CARBIDE (USA), WACKER (Germany), RHONE-POULENC (France) and others.

As preferred liquid silicones SYLGARD 182 and 184 from DOW
20 CORNING and RHODORSIL RTV from RHONE-POULENC have been used. At room temperature these silicones harden in some hours and of course much faster at higher temperatures. For RHODORSIL RTV 141 A and RTV 141 B typical hardening times would be at 65°C- 4 hours, at 100°C- 1 hour and at 150°C-
25 0,5 hours

As filler zeolites, e.g. type 3A, 4A, 5A or 13X could be used as well as other types of absorbents like aluminumphosphates, activated alumina or silica gel. The
30 primary particle size of this type of filler would be around 0,5 to several microns.

Zeolites of type A are alkali alumino-silicates of the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. While zeolites of
35 the type X are alkali alumino-silicates of the general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2,5 \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$.

A zeolite of type 3A, e.g. would adsorb molecules in the center hole with a kinetic diameter up to 3 Angström and so on.

5

Another type of filler is so called fumed silica. Commercially available products of this kind are marketed under the name AEROSIL by the company DEGUSSA AG (Germany). Several fillers of this type have been tested, like for instance hydrophilic AEROSIL types with relatively low surface area:

	AEROSIL	OX 50	surface area	50m ² per g
	AEROSIL	MOX 80	surface area	80m ² per g
15	AEROSIL	MOX 90	surface area	90m ² per g

Hydrophilic AEROSIL types with high surface area which have been tested are:

20 AEROSIL 130,150, 200,300,380.

These latter types have a disadvantage at higher filler percentages due to pronounced thickening effect. Larger amounts of solvents have to be used in order to allow the application of membrane formulations using these fillers.

25

The primary particle size for this type of filler would be 0.007 to 0.04 microns and the associated particle size in the range of 1 to 10 microns.

30

In order to achieve the properties of a membrane which could be used in the method according to the invention quite high percentages of filler are needed. It has been found that with zeolites and similar adsorbents, as well as fumed silica, between 30 and 90 percent would be appropriate. The range 50 to 80 percent is preferred.

35

The inventive idea resides in the physical modification of the PDMS used as membrane forming agent by means of an active filler which limits the gas or air loss without
5 significantly reducing the water vapor permeation.

The characteristic of these types of adsorbing material which is normally used, e.g. in the known adsorption dryers according to the above, resides in their ability to adsorb
10 in their center hole molecules of certain sizes. The corresponding number in the designation of the zeolite reflects the size of a molecule which could be adsorbed.

It exist types of Munters dryers, in which silica-gel is
15 used to take out the largest part of the water from the air and a zeolite is used to take care of the remaining portion of the water, to achieve a low dew point. The water adsorbed by the zeolite will then be strongly bound.

20 However, for the purpose of this invention the outside surface of the larger particles is also essential in its interaction with the water vapor. Water molecules adsorbed in a monomolecular layer in the center holes are very strongly bound to the crystals and the energy needed to
25 desorb the water vapor is quite high. For the water adsorbed at the surface of the particles, or in the case of zeolites with larger center holes like e.g. type 13X or 5A, in a second or even third layer within the hole, the energy to desorb this water is much lower.

30

Thus, when the adsorbed water in the membrane according to the invention is exposed to a decreased partial pressure the first, and in some cases the only, water which is removed is the weakly adsorbed water. The continuous
35 desorption in the membrane which creates the flow of water through the same could be explained by this mechanism.

When the percentage of filler of the discussed type , especially the fumed silica, is increased it is a well known fact that the mechanical properties of the thus
5 modified PDMS are improved in relation to the unmodified PDMS, to start with. Above a certain percentage of filler the mechanical properties are then declining again down to the level of the unmodified PDMS to reach levels below this.

10

Additionally, the filler could be considered to have both an active and a passive effect on the permeation of water vapor and air respectively.

15 Hydrophilic zeolites and fumed silica have polar groups e.g. OH-groups on the surface of the particles. The water is interacting with these polar surface-groups which creates a preferential transport of the water vapor along the filler-PDMS interface. This is the active effect which
20 would increase with increasing percentage of filler in the PDMS.

On the other hand the oxygen and nitrogen of the air which mainly diffuses through the unmodified PDMS will not
25 interact with the polar groups on the surface of the particles but will see an obstacle for the diffusion in each particle. This means that a higher percentage of filler in the PDMS will more efficiently decrease the permeation of the air through the membrane which means that
30 the passive effect of the filler is increasing with higher percentages as well.

When membranes are modified in order to achieve higher selectivity in a separation process this is generally
35 coupled to a loss of flux. As can be seen from the above the combination of the method and membrane according to the

invention makes it possible to raise the selectivity (water vapor-air) as well as maintaining an acceptable water flux or even increasing the flux rate at a working point on the characteristic for the mechanical properties vs. filler-
5 content above or close to values for the unmodified PDMS.

For very high percentages of filler, problems might arise to get a tight membrane without pinholes and other microscopic defects. In such cases and even for somewhat
10 lower percentages it could be of advantage to add a further layer of preferably unmodified PDMS to close pinholes and protect the surface.

Said membrane can be applied in form of spiral wound
15 modules or hollow fiber modules. In the application form of a spiral wound module, the flat composite membrane is rolled up together with appropriate spacer materials according to known methods.

20 In the application form of hollow fibres, the microporous hollow fibre supports are produced by means of state of the art methods and coated with the filler-PDMS-solvent formulation by dipping the hollow fibre into an appropriate bath.

25 In case of hollow fibre modules the modules could be prefabricated including the membrane supports and then be flushed with the membrane formulation, preferentially on the inside of the fibres.

30 The invention also concerns a process for the manufacture of the membranes according to the invention. The technical problem resides in the combination of making a membrane with good mechanical properties despite a high or very high percentage of filler needed to achieve the special
35 permeation properties and the required homogeneity. The

application of the filler material to the membrane forming agent is crucial.

When using zeolites and similar adsorber materials as fillers in the membrane the preferred commercially available products in powder form have a primary particle size in the order of 1 micron. As mentioned above these small particle, large active surface materials are agglomerated due to considerable internal forces between the particles. Due to the fact that the final thickness of the membrane layer sometimes will be less than the diameter of the agglomerates, it is essential to break up the agglomerates. The process according to the invention specifies in a preferred embodiment wet-milling, which is a known method per se, of the powder in order to obtain adsorber particles in the order of 1 micron. The wet milling could be carried out in a solvent like hexane or heptane in for instance a ball-mill made from abrasion resistant ceramic. Heptane is preferred because of higher boiling point which means slower evaporation during the milling operation.

In a preferred embodiment the wet-milling or at least the final part of the same is carried out in the solution of the membrane forming liquid silicone plus a solvent like heptane or hexane.

When using fumed silica and similar adsorber materials as fillers in the membrane, wet-milling could also be used in order to break up the agglomerates. In this case, however, a high speed agitator would be sufficient for the same purpose in stead of the ball mill.

The wet-milling and high speed agitation respectively will have the effect on the agglomerates that they disintegrate and the wet state helps to stabilize the primary particles,

especially if the milling process is carried out in the presence of the polymer, which gives the very fine distribution needed to achieve the homogeneous, thin membrane. The polymer has in this case the effect of a
5 protecting colloid. This homogeneous distribution is especially important if the membrane formulation is subsequently diluted for the dipping process.

Thus, by means of the process steps according to the above
10 the liquid membrane coating formulation typically contains a wet milled active filler, a silicone polymer, e.g. polydimethylsiloxane, an appropriate hardener, a solvent, preferably heptane and in some examples a coupling agent, such as bifunctional silanes.

15

This formulation is now used to achieve the membrane coating on the appropriate support by means of a known method such as dipping or casting.

20

25

CLAIMS

5 1 Method for drying of gases, especially compressed air,
by means of a membrane having a thin membrane coating with
a certain separation factor (water vapor - gas) arranged
on a membrane support whereby gas or air containing water
in vapor form is applied to one side of the membrane, the
10 feed side, and due to the separation factor mainly water
vapor is permeating to the other side of the membrane, the
permeate side,

characterised in that

15

a fraction of the gas or air stream, is arranged to
permeate through the membrane from the feed side to the
permeate side, in order to transport permeated water vapor
20 away from the permeate side of the thin membrane coating
and through the membrane support, thereby creating and
maintaining a water vapor partial pressure difference
between the feed side and the permeate side of the thin
membrane coating, which constitutes the driving force for
25 the permeation of the water vapor through the membrane.

2 A membrane for drying of gases, especially compressed
air, by means of the method according to claim 1,
comprising a thin membrane coating, such as a crosslinked
5 polydimethylsiloxane, a membrane support of a chemically
and mechanically resistant micro-porous polymer material,
such as an ultrafilter or microfilter of polyamide,
polypropylene, polysulfone or polyethersulfone,

10 characterised in that

said membrane coating comprises 30-90 % of a high surface
area filler which acts as a selective diffusion barrier to
the gas or air and water-vapor.

15

3 A membrane according to claim 2,

characterised in that

20 said membrane support is an ultrafiltration membrane having
a diameter of the pores in the range of 10 000 to 1000 000
daltons.

4 A membrane according to claim 2,

25

characterised in that

said membrane support is a microfilter having a diameter of
the pores in the range of 0,01 to several microns,
30 preferably 0,01 to 1 micron.

5 A membrane according to any of the claims 2-4

characterised in that

5

said high surface area filler is chosen from the group zeolites, aluminophosphates, activated alumina or silica gel having a particle size in the range of 0,5 to several microns.

10

6 A membrane according to claim 5,
characterised in that

15 said active filler is zeolite 3A, potassium-aluminium-silicate (sodalite structure) or zeolite 4A, sodium--aluminium-silicate (sodalite structure) or zeolite 5A, calcium-aluminium-silicate (sodalite structure) or zeolite 13X, sodium-aluminium-silicate (faujasite structure).

20 7 A membrane according to any of the claims 2-4

characterised in that

25 said high surface area filler is a so called fumed silica like AEROSIL

8 A membrane according to claim 7

characterised in that

30

the primary particle size of the fumed silica is in the range of 5 to 50 nm.

9 A membrane according to any of the claims 2-7

characterised in that

5

an additional coating of preferably unmodified PDMS is applied to one side of the membrane.

10 A process for the manufacturing of a membrane according to any of the claims 2-9 comprising the steps of preparing a membrane forming liquid including an active filler and applying the same on an appropriate support by means of a dipping or casting process known per se

15 characterised in that

in order to break apart the agglomerations of the active filler due to the internal forces between the particles of the filler, said filler is mixed with at least part of the membrane forming liquid in a wet-milling process.

11 A process according to claim 10

characterised in that

25

said part of the membrane forming liquid comprises a solvent.

12 A process according to claim 10

30

characterised in that

said part of the membrane forming liquid comprises a membrane forming liquid silicone plus a solvent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/01610

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: B 01 D 53/26, B 01 D 53/22, B 01 D 69/14, B 01 D 67/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System |

Classification Symbols

IPC⁵ : B 01 D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A, 0323431 (PERMEA INC.) 5 July 1989 see claim 1 --	1
Y	FR, A, 2079460 (RHONE-POULENC) 12 November 1971 see the whole document cited in the application	1
A	--	2,5,6,9-12
A	EP, A, 0254758 (SETEC) 3 February 1988 see page 2, line 39 - page 3, line 49 cited in the application --	2,5,6
A	US, A, 4230463 (J.M.S. HENIS) 28 October 1980 see column 21, lines 8-43 cited in the application --	2
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IV. CERTIFICATION

Date of the Actual Completion of the International Search

17th August 1990

Date of Mailing of this International Search Report

18. 09. 90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. SOTELO

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 8901610

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